



High-performance self-humidifying membrane electrode assembly prepared by simultaneously adding inorganic and organic hygroscopic materials to the anode catalyst layer

Huagen Liang^{a,b,c}, Dai Dang^{a,b,c}, Wang Xiong^{a,b,c}, Huiyu Song^{a,b,c}, Shijun Liao^{a,b,c,*}

^aThe School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

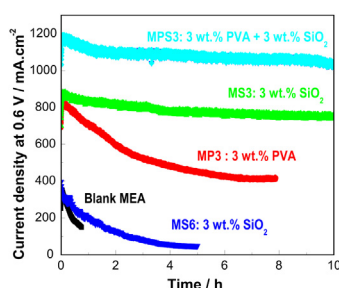
^bThe Key Laboratory of Fuel Cell Technology of Guangdong Province, Guangzhou, Guangdong 510640, China

^cThe Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, Guangzhou, Guangdong 510640, China

HIGHLIGHTS

- A self-humidifying MEA is prepared by adding both PVA and silica to the anode layer.
- The MEA shows excellent self-humidification performance at 60 °C and under 15% RH.
- Good self-humidification stability is confirmed by a 30 h long term experiment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 January 2013

Received in revised form

6 April 2013

Accepted 11 April 2013

Available online 7 May 2013

Keywords:

Proton exchange membrane fuel cell

Membrane electrode assembly

High-performance

Self-humidifying

Polyvinyl alcohol

Silica

ABSTRACT

A novel self-humidifying membrane electrode assembly (MEA) has been successfully prepared by adding both a hydrophilic organic polymer (polyvinyl alcohol, PVA) and an inorganic oxide (silica) to the anode catalyst layer. This MEA shows excellent self-humidification performance under low-humidity conditions. A sample containing 3 wt.% PVA and 3 wt.% silica in the anode catalyst layer achieves a current density as high as 1100 mA cm⁻² at 0.6 V, and the highest peak power density is 780 mW cm⁻², operating at 60 °C and 15% relative humidity for both anode and cathode. The sample also shows excellent stability at low-humidity: after 30 h of continuous operation under the same conditions, the current density decreases just slightly, from 1100 mA cm⁻² to ca. 900 mA cm⁻², whereas with MEAs to which only PVA or silica alone had been added, the current densities after 30 h is just 700 mA cm⁻² and 800 mA cm⁻², respectively. The improved self-humidification performance can be attributed to the synergistic effect of two hygroscopic materials in the anode catalyst layer.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is recognized as a promising alternative to traditional energy sources because of its

impressive features, including low or zero polluting emissions, high energy density, high conversion efficiency and silent discharge [1,2].

Although PEMFCs offer several advantages, obstacles such as water management, cost and durability still prevent their commercialization [3–5]. Nafion membrane is a key component of PEMFCs, commonly applied to the electrolyte because of its good mechanical and thermal stability, as well as its high proton conductivity at 100% relative humidity (RH) [6,7]. Nafion is also used in

* Corresponding author. The School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China. Tel./fax: +86 20 8711 3586.

E-mail address: chsjliao@scut.edu.cn (S. Liao).

the catalyst layer as a binder and proton conductor. However, the proton conductivity of Nafion depends strongly on the water content; dehydration of the Nafion membrane will lead to a series of detrimental effects on the PEMFC's performance. For example, the proton conductivity of Nafion membrane will decrease and the ohmic resistance of the cell will increase under low-humidity conditions, causing rapid decay in cell performance [8,9]. Thus, in terms of the actual operating conditions of a PEMFC, an external humidifier has been used to maintain the water content of the cell system. In other words, the reactant gas must pass through the external humidifier and absorb water vapor before entering the cell. However, this approach complicates the cell system and reduces its energy efficiency and volume efficiency, as well as increasing its cost, thereby hindering commercialization. Indeed, the development of a self-humidifying membrane electrode assembly (MEA) has become one of the most important subjects in the PEMFC field.

Great efforts have been made to overcome problems arising from dehydration, through modifying and developing either the PEM or the MEA structure [6–8,10–15]. Incorporating a hydrophilic inorganic oxide into the PEM is an effective method to improve the water-retaining capacity of PEMFCs at high temperatures [16–21]. As early as the 1990s, Watanabe et al. [16–18] reported this type of composite membrane, recasting a solubilized Nafion ionomer containing Pt nanoparticles and hygroscopic inorganic oxides (SiO_2 or TiO_2). In this composite membrane, the Pt nanoparticles are expected to suppress reactant crossover by the catalytic recombination of crossover hydrogen with oxygen (which can reduce the cell's circuit polarization), and the hygroscopic inorganic oxides are expected to absorb the water produced at Pt particles and at the cathode reaction, thereby maintaining the water level for appropriate proton conductivity in the membrane. However, many defects remain: (1) the process is complicated and costly, (2) Pt nanoparticle dispersion in the membrane is not uniform, which may lead to local electronic conduction and consequent cell self-discharge or even failure, and (3) the proton conductivity of the composite membrane is less than that of a pure Nafion membrane because the inorganic oxide cannot conduct protons. Many researchers have improved upon this method, such as by adding other hydrophilic materials with proton conductivity (heteropoly acid, sulfated zirconia, zirconium phosphate, or Pt/sulfated multi-walled carbon nanotubes) to the membrane instead of an inorganic oxide [9,22–27].

Other methods to prepare self-humidifying MEAs are to add hygroscopic material directly into the catalyst layer, to use a self-humidifying catalyst, or to optimize the MEA's structure so as to make it self-humidifying [28–32]. Our group successfully prepared a novel self-humidifying catalyst, Pt/ SiO_2 /C [28,29]. When this catalyst was used in the anode layer, excellent performance in low-humidity conditions resulted. A detailed description of the cell performance achieved by mixing SiO_2 with a catalyst under different humidity conditions was reported by Senthil Velan [30]. Cindrella et al. [33] designed a self-humidifying MEA by adding a layer between the catalyst layer and the gas diffusion layer (GDL) to improve the low-RH performance of PEMFCs.

Preparation of a self-humidifying MEA by adding a hydrophilic organic polymer to the catalyst layer has rarely been reported. Cindrella and Kannan [34] incorporated an interlayer of polyaniline (PANI) between the catalyst layer and the GDL to improve the low-RH performance of PEMFCs. Huang et al. [35] achieved better results when they placed a layer of polyaniline nanofibers (PANFs) between the anode catalyst layer and the GDL than when they placed a PANFs layer between the membrane and the anode catalyst layer, or coated the catalyst layer with PANFs and catalyst slurry. Kitahara et al. [36] developed a new hydrophilic and

hydrophobic double microporous layer (MPL) coated GDL, and achieved further performance enhancement without humidification at the cathode. The hydrophobic MPL, which consisted of carbon black and PTFE, was coated on a carbon paper substrate. The hydrophilic layer, comprised of carbon black and polyvinyl alcohol (PVA), was coated on the hydrophobic MPL. The hydrophilic layer was effective for conserving humidity on the cathode layer. Recently, we reported a self-humidifying MEA fabricated by the addition of PVA to the anode catalyst layer [37]. The current density at 0.6 V and 0.7 V reached 1000 mA cm^{-2} and 600 mA cm^{-2} , respectively, when the cell was operated at 50°C , 30 psi back-pressure, and 34% RH for the anode and cathode. After 60 h of constant voltage testing, the current density at 0.6 V remained at $750\text{--}780 \text{ mA cm}^{-2}$, revealing the excellent self-humidifying capacity of PVA.

Although great progress has been achieved in recent years, much work still needs to be done to improve the performance of PEMFCs under low-humidity conditions. In this study, we first prepared a new type of self-humidifying MEA by introducing a hydrophilic organic polymer (PVA) and a hydrophilic oxide (silica) into the anode catalyst layer simultaneously; the resulting MEA exhibited better self-humidifying performance at a cell temperature of up to 60°C . To our knowledge, this is the first report of such excellent self-humidifying performance at such a high temperature.

2. Experimental

2.1. Preparation of membrane electrode assemblies

Prior to fabricating the MEAs, Nafion 212 membranes were pretreated by boiling them in a 5 wt.% peroxide solution at 80°C for 1 h, then in a 0.5 M sulfuric acid solution at 80°C for 1 h, followed by washing with deionized water. Finally, the processed Nafion membranes were stored in deionized water for later use.

Commercial HiSPEC 4100 Pt/C (40 wt.% Pt, Johnson Matthey) was used for both anode and cathode, and the catalyst inks were prepared by adding catalyst and 5 wt.% Nafion ionomer solution (DuPont, USA) into the isopropanol solvent.

To prepare the anode catalyst layer, PVA (Sinopharm Chemical Reagent Co., Ltd., China) and silica were added to the ink to obtain a hydrophilic anode catalyst layer. Unless otherwise specified, the PVA and silica measured 3.0 wt.% in the anode catalyst layer. The cathode catalyst ink was prepared by the same process but without adding any hydrophilic materials. The dry Nafion content in the anode and cathode catalyst layers was adjusted to 25 wt.%. The Pt loadings for the anode and cathode were 0.1 mg cm^{-2} and 0.2 mg cm^{-2} , respectively. The anode and cathode catalyst layers were prepared by a catalyst-sprayed membrane method, previously reported by our group [38]. For comparison, two other MEAs, with only PVA or only silica in the anode catalyst layer, were prepared using the same method. The active area of each MEA was 5 cm^2 .

Table 1
Specifications of the MEAs prepared in this study.

MEA	Anode ($0.1 \text{ mg Pt.cm}^{-2}$)	Cathode ($0.2 \text{ mg Pt.cm}^{-2}$)
Blank MEA	Pt/C, Nafion	Pt/C, Nafion
MP3	Pt/C, Nafion, 3 wt.% PVA	Pt/C, Nafion
MS3	Pt/C, Nafion, 3 wt.% silica	Pt/C, Nafion
MS6	Pt/C, Nafion, 6 wt.% silica	Pt/C, Nafion
MPS1	Pt/C, Nafion, 1 wt.% PVA + 1 wt.% silica	Pt/C, Nafion
MPS3	Pt/C, Nafion, 3 wt.% PVA + 3 wt.% silica	Pt/C, Nafion
MPS5	Pt/C, Nafion, 5 wt.% PVA + 5 wt.% silica	Pt/C, Nafion
MPS7	Pt/C, Nafion, 7 wt.% PVA + 7 wt.% silica	Pt/C, Nafion

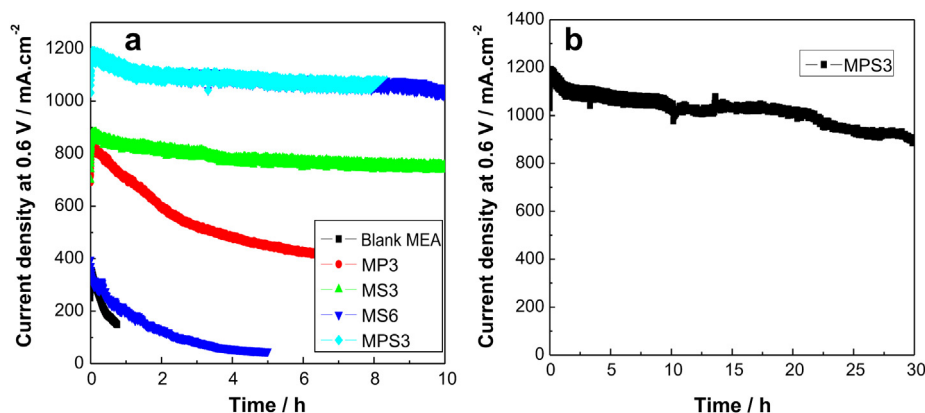


Fig. 1. Performance of various MEAs at 0.6 V with the addition of different hydrophilic materials to the anode catalyst layer (a) and the long-term discharge curve of MPS3 (b), all at 15% RH both for anode and cathode. Cell temperature was 60 °C, both backpressures for air and hydrogen were 30 psi, and hydrogen and air flow rates were 300 and 800 mL min⁻¹, respectively.

Table 1 shows the anode and cathode compositions of all nine MEAs. For simplicity, these MEAs are denoted as MPS0, MP3, MS3, MS6, MPS1, MPS3, MPS5, MPS7, and MPS10.

2.2. Preparation of the gas diffusion layer

The gas diffusion layer used for this study was prepared by following procedures, firstly, carbon paper (TGP-H-060, Toray) was impregnated with a diluted PTFE solution (60%, Aldrich), followed by drying and calcining at 400 °C for 30 min to make the PTFE infiltrated in the carbon paper, the loading of dry PTFE is ca. 15 wt.%. Secondly, a microporous layer was prepared by spraying a homogeneous slurry composed of diluted PTFE and carbon powder (Vulcan® XC72, Cabot, USA) onto the PTFE loaded carbon paper, followed by calcining at 400 °C for 30 min. The loading amount of carbon powder on the carbon paper substrates is 3 mg/cm² and the PTFE content in microporous layer is ca. 15 wt.%.

2.3. Single-cell tests

A single cell was assembled with the as-prepared MEAs and two GDLs without hot pressing, and the performance was recorded using a Fuel Cell Testing System (Arbin Instruments, USA). Pure hydrogen and compressed air were fed to the anode and cathode, respectively, at flow rates of 300 and 800 mL min⁻¹. Before the performance test, the cells were activated in a continuous discharge mode until stable performance was obtained; the activation was

processed at a cell temperature of 70 °C and with 100% humidification of the hydrogen and air.

The cell performance at various RH levels was measured at a cell temperature of 60 °C, with the backpressures of both hydrogen and air at 30 psi. The temperatures of the gas lines to the anode and the cathode were always set at 5 °C above the humidification temperatures to prevent water condensation.

2.4. Electrochemical measurements

The polarization resistance of the single cells was investigated with electrochemical impedance spectroscopy using a Zahner IM6e electrochemical workstation (Zahner, Germany) at 0.8 V in potentiostatic mode. A signal amplitude of 5 mV in the frequency range of 100 mHz–1000 Hz was applied.

2.5. Measurement of water uptake in the anode catalyst layer

Measurement of water uptake was performed as described in our previous report [37].

3. Results and discussion

Fig. 1(a) compares the self-humidification performance of three MEAs with different hydrophilic materials added to the anode catalyst layer—MP3 with 3 wt.% PVA, MS3 with 3 wt.% silica, MS6

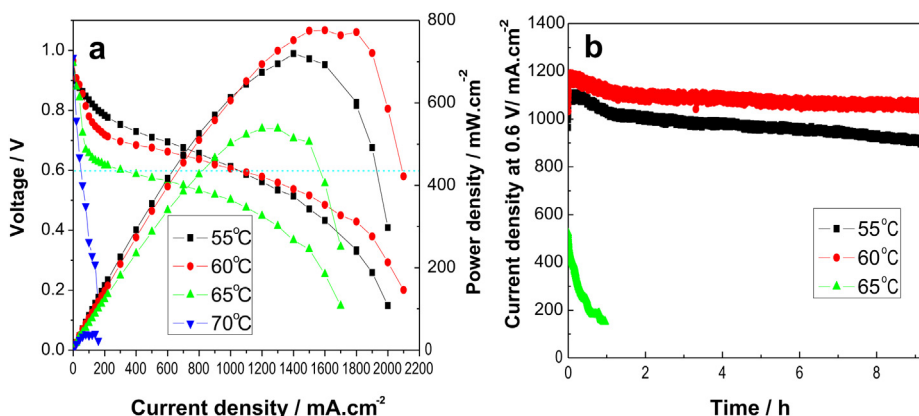


Fig. 2. Polarization curves and power outputs (a) and long-term testing performance (b) of the MPS3 MEA operated at different cell temperatures under 15% RH for both anode and cathode, and at a backpressure of 30 psi for both anode and cathode.

with 6 wt.% silica, and MPS3 with 3 wt.% PVA and 3 wt.% silica—as well as a blank MEA.

Under 15% RH for both anode and cathode, it is clear that the performance of the blank MEA decreased rapidly, the current density at 0.6 V dropping from 350 mA cm⁻² to less than ca. 120 mA cm⁻² within 1 h, indicating the blank MEA was not self-humidifying.

As Fig. 1(a) indicates, the MEA with 3 wt.% silica showed good self-humidification performance and stability; its current density at 0.6 V reached 900 mA cm⁻² and stabilized at 750 mA cm⁻² after 10 h of operation. However, sample MS6, containing 6 wt.% silica, exhibited poor performance, perhaps due to the addition of too much non-proton-conducting silica.

It is clear that adding only PVA can result in self-humidification. The initial current density of sample MP3 at 0.6 V was 800 mA cm⁻²; however, this rapidly decreased to 400 mA cm⁻² within 10 h, implying that adding only PVA will not yield stable self-humidification.

But it is interesting that excellent self-humidification performance could be achieved by adding both inorganic silica and organic PVA to the anode catalyst layer. In the case of sample MPS3, adding 3 wt.% PVA and 3 wt.% silica resulted in excellent self-humidification at low humidity: the current density at 0.6 V reached 1100 mA cm⁻², and after operation for 10 h the current density stabilized at 1000 mA cm⁻².

It should be pointed out that the MPS3 achieved excellent activity and stability at 60 °C, which is a very high cell temperature for self-humidifying MEAs. As reported previously [28,29,39–41] and as shown in Fig. 1(a), when only a hydrophilic inorganic substance was added, the self-humidification performance of the MEA degraded quickly at such a high cell temperature. Our results make it possible for self-humidifying MEAs to be applied practically.

Furthermore, we conducted a long-term self-humidification test for MPS3, as shown in Fig. 1(b). The test was performed at 60 °C and under 15% gas humidification both for anode and cathode. At such a high cell temperature and low humidification, the current density of MPS3 at 0.6 V remained as high as 900 mA cm⁻² after 30 h of testing, indicating the excellent self-humidification performance and stability of this type of MEA. Although the attenuation degree of the current density was 18%, this performance was much better than previously reported [37]. To our knowledge, MPS3 is the first MEA with such excellent self-humidifying performance at this high cell temperature.

Fig. 2(a) shows the effects of cell temperature on the performance of MPS3 at a low RH of 15%. It is clear that a temperature too high or too low will result in poor self-humidification; the optimal cell temperature for the MPS3 MEA seems to be 60 °C, a finding also supported by the long-term testing results presented in Fig. 2(b).

Table 2

Ohmic resistance (R_{Ω}) and charge transfer resistance (R_{ct}) of the four MEAs under different RHs.

Resistances of MEAs (Ω cm ⁻²)	100% RH		60% RH		35% RH		15% RH ^a	
	R_{Ω}	R_{ct}	R_{Ω}	R_{ct}	R_{Ω}	R_{ct}	R_{Ω}	R_{ct}
Blank MEA	0.45	0.27	0.46	0.32	0.59	0.77	0.95	0.75
MP3	0.32	0.29	0.44	0.36	0.53	0.69	0.88	0.78
MS3	0.35	0.28	0.38	0.29	0.46	0.8	0.76	0.74
MPS3	0.25	0.27	0.26	0.32	0.31	0.61	0.72	0.7

^a The electrochemical resistance of each single cell was measured at 0.7 V under 15% RH, but at 0.8 V for the other RHs.

The inferior performance of MPS3 at 55 °C compared with at 60 °C may be caused by the kinetics factor, with a lower temperature resulting in lower kinetics performance. However, we think the inferior performance at 65 °C and 70 °C may have been caused by the poor conductivity of the membrane and catalyst layers due to water loss at these higher temperatures.

We also compared the performance of the four MEAs under full humidification and 15% RH, respectively. As shown in Fig. 3(a), when the MEAs were at 100% humidification, in the low current density area all those with hydrophilic materials added to the catalyst layer showed inferior performance compared to the blank MEA, which may have resulted from the increase in resistance due to the addition of hydrophilic materials. However, in the high current density area, all the self-humidifying MEAs yielded superior performance compared with the blank MEA. We speculate that the self-humidifying MEAs may have had better water balance than the blank one.

As shown in Fig. 3(b), at 15% RH all the self-humidifying MEAs performed much better than the blank in both low and high current areas; particularly in the high current area, the MPS3 showed far superior performance to all the other MEAs. These results further demonstrate that adding hygroscopic material to the anode catalyst layer can enhance MEA performance under low humidification, and adding both inorganic and organic hygroscopic materials simultaneously to the anode catalyst layer especially enhances MEA performance under that condition.

To understand the mechanism of the four MEAs' self-humidification performance, we measured their in situ electrochemical impedance at various RH levels. Table 2 shows the ohmic resistance (R_{Ω}) and the charge transfer resistance (R_{ct}) of the four MEAs. It is clear that in relation to the blank MEA, the ohmic resistance for all of them decreased significantly at every RH value; in particular, the MPS3 MEA exhibited the least resistance throughout. These results are quite consistent with the performance results, as

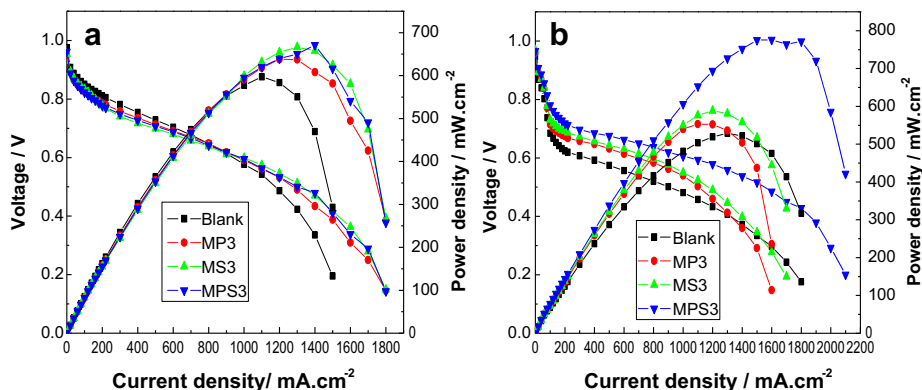


Fig. 3. Performance comparison of MEAs with different additives. Single cells operated at 60 °C and 30 psi backpressure, under 100% RH (a) and 15% RH (b) for both anode and cathode.

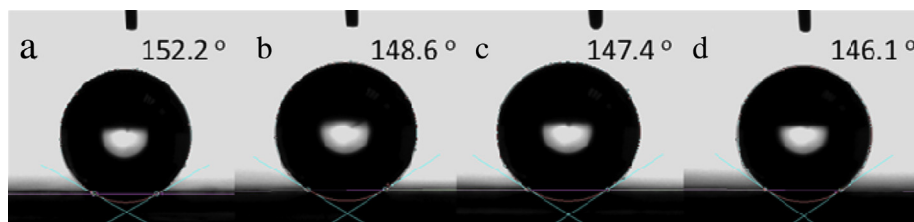


Fig. 4. Contact angles of 5 mL pure water droplets with blank MEA (a), MP3 (b), MS3 (c), and MPS3 (d), measured using an OCA 40 Video-Based Optical Contact Angle Meter (Dataphysics, Germany).

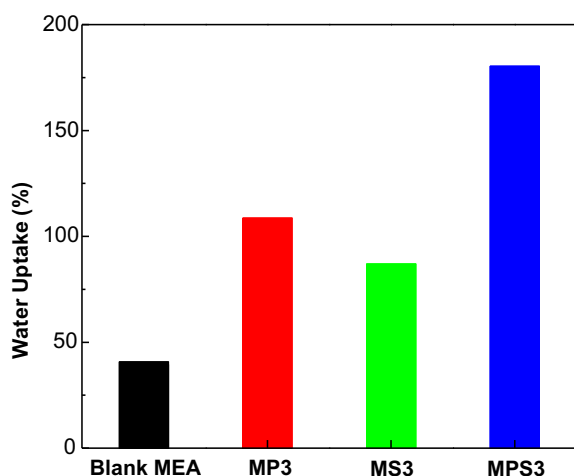


Fig. 5. The water uptake of various MEAs, three of which had different hygroscopic materials added to the anode catalyst layer.

lower resistance results in better self-humidification. We believe the good conductivity of the MEAs with added hydrophilic materials was caused by their effective water retention. It is important that the charge transfer resistance was almost unaffected by the hydrophilic materials; at 100% and 60% RH, all the MEAs with added hydrophilic materials had almost the R_{ct} as the blank MEA, but at low RH levels (35% and 15%), the MPS3 MEA showed a slightly lower R_{ct} than the blank, MP3, and MS3 MEAs. Thus, we can conclude that the addition of hydrophilic materials did not affect the charge transfer process very much.

It should be pointed out that the R_{Ω} and R_{ct} values of MP3 and MS3 are larger than those of MPS3 at each RH, implying that the

MEA containing both PVA and silica in the anode catalyst layer may have better water retention than the MEAs with either PVA or silica alone. In summary, increasing the wettability of the anode catalyst layer will increase the proton conductivity of the Nafion electrolyte, facilitating the electrochemical reaction at the electrode [41].

In addition, both the R_{Ω} and the R_{ct} increased as the RH dropped from 100% to 15%; an especially sharp increase occurred when the RH changed from 60% to 35%. This reveals that humidification not only influenced the ohmic resistance of the electrolyte through affecting the proton motion, but also had an impact on the charge transfer resistance by affecting the transfer of electrons at the interface.

To further understand the mechanism of self-humidifying MEAs, the wetting properties of the four were measured by contact angle measurement. Fig. 4 shows the anode catalyst layer contact angles of the prepared MEAs with different hygroscopic materials. Clearly, with the addition of hydrophilic materials, the contact angle decreased; the blank MEA had the biggest angle and the MPS3 had the smallest, revealing that adding hydrophilic materials can improve the water retention capacity of MEAs.

Because the Nafion ionomer in the catalyst layer and the Nafion membrane both need enough water to maintain high proton conductivity, especially under low humidity, the water uptake of the anode catalyst layers containing different hydrophilic materials was measured, as shown in Fig. 5. It can be seen that the water retention of the anode catalyst layer was improved significantly by adding hygroscopic materials. The water uptake of MPS3 was three times higher than that of the blank MEA and twice that of MS3, revealing that the addition of both inorganic and organic polymer hydrophilic materials remarkably improved the water uptake of the anode catalyst layer, and this enhanced water retention may be the most important reason for the excellent self-humidifying performance of MPS3.

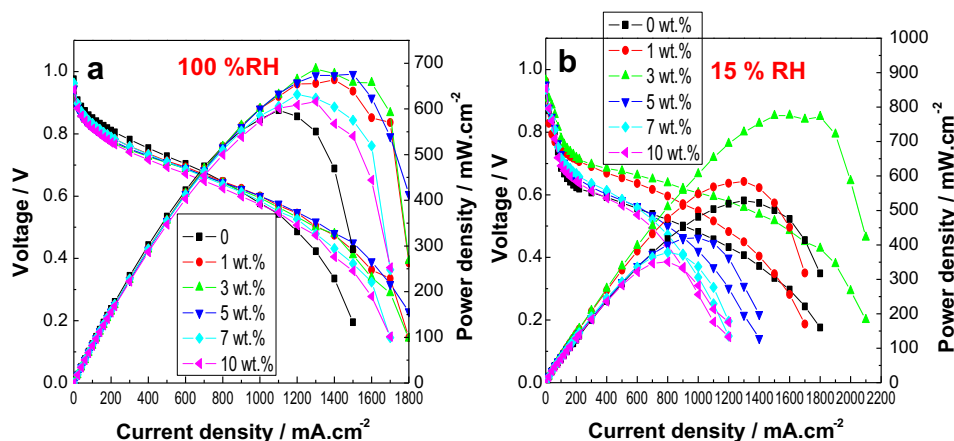


Fig. 6. Polarization curves and power outputs of the MEAs containing various amounts of PVA and silica. The single cells were operated at 60 °C and 30 psi backpressure, at 100% RH (a) and 15% RH (b) for the anode and cathode.

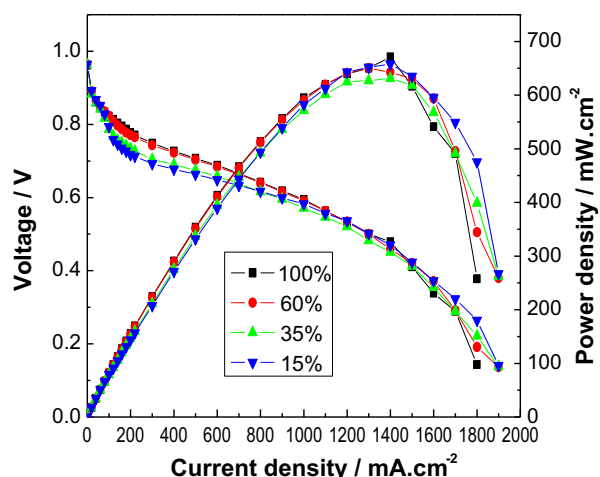


Fig. 7. Polarization curves and power outputs of the MPS3 MEA operated under different relative humidities at a cell temperature of 60 °C and a backpressure of 30 psi.

Fig. 6 plots the polarization curves and power outputs of the MEAs with various amounts of PVA and silica in the anode catalyst layer, under 100% RH (a) and 15% RH (b). The variation in cell performance is similar to that presented in Fig. 3; compared to the blank MEA, at 100% RH MEAs containing hydrophilic materials demonstrated inferior performance in the low current area but superior performance in the high current area. However, at 15% RH, the MEAs with hydrophilic additives showed superior performance to the blank MEA in both low and high current areas, and MPS3 performed best. It seems that the optimal PVA and silica content in the anode catalyst layer is 3 wt.%. More than this decreases performance because both PVA and silica are non-conductive materials, so adding too much of them will lower the conductivity of the anode catalyst layer. As shown in Fig. 6(b), the performance of MPS5, MPS7, and MPS10 was much worse than that of the blank MEA at 15% RH.

To further investigate the effects of humidification on the MPS3 MEA, we measured its performance at various RHs. From Fig. 7 we can see that almost no difference in its performance was observable when the RHs of both anode and cathode were changed from 100% to 60%. Once the RH was decreased to 35% and 15%, reduced performance was evident in the low discharge current density region. However, almost no decline in performance was observable in the high discharge current density region, confirming the excellent self-humidification property of MPS3.

4. Conclusions

In summary, a novel, high-performance, self-humidifying MEA was prepared by adding two hygroscopic materials—PVA and silica—to the anode catalyst layer. This MEA displayed excellent performance at 15% RH and a very high cell temperature of 60 °C, revealing its impressive self-humidification properties and making its practical use possible. We suggest that the simultaneous addition of inorganic and organic polymer hydrophilic materials (1) enhanced the various MEAs' water uptake and retention, (2) improved their wettability, (3) thereby resulted in lower ohmic resistance and even lower charge transfer resistance, and (4) finally

led to their high self-humidifying performance. The results of this work may provide a facile and effective way to realize self-humidifying MEAs for practical PEMFC applications.

Acknowledgments

The authors gratefully acknowledge the NSFC of China (Project Numbers 21276098 and 21076089) for financial support of this work.

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